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TRANSITION DENSITY OF STATES (TDOS) OF THE $\text{Si}(100)2 \times 1$ SURFACE DERIVED FROM THE $\text{L}_{2,3}\text{VV}$ AUGER LINESHAPE COMPARED WITH CLUSTER CALCULATIONS

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The termination of a silicon crystal along the (100) orientation resulting in a 2×1 reconstructed surface induces relatively large variations in the local density of states (LDOS) of the different types of surface atoms, such as the up and down dimer atom and the backbond atom. Auger electron spectroscopy (AES) is able to probe the LDOS of the silicon atom in which the $\text{L}_{2,3}$ core hole has been created and is therefore a candidate to analyze the LDOS of the surface atoms. A detailed analysis of the $\text{SiL}_{2,3}\text{VV}$ Auger electron spectrum allows us to determine a high quality transition density of state (TDOS) of the $\text{Si}(100)2 \times 1$ reconstructed surface. The resolved peaks in the TDOS were compared with previous AES, UPS and EELS measurements reported by other investigators. Quantum chemical cluster calculations were used for the interpretation of the TDOS in the actual p-like and s-like partial local density of states for different types of silicon atoms. These quantum chemical cluster calculations of the partial LDOS localized at atoms of the $\text{Si}(100)2 \times 1$ surface were found to be in agreement with other types of calculations. Comparing the experimental and the calculated DOS we were able to distinguish several new peaks in the TDOS obtained with AES and to discriminate features in the experimentally obtained TDOS into local electron distributions localized at different surface atoms.

1. Introduction

Auger electron spectroscopy (AES) is a widely used technique for surface chemical element analysis [1]. Earlier studies [2–12] showed that analysis of the lineshape of the core–valence–valence (CVV) Auger spectrum can provide information of the local chemical environment of the target atomic species. However, the CVV Auger intensity $N(E)$ becomes distorted by all kinds of losses such as elastic and inelastic scattering, interaction with collective oscillations (plasmons, etc.) and instrumental broadening [13–16]. It is well established that corrections of these Auger line-profile distortions [16–19] are of sufficient quality to compare these results with theory as developed by

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Feibelman et al. [3] and Jennison [20,21]. Nevertheless incompatibility of the theoretical lineshape and the corrected measured Auger CVV lineshape in several materials still remains [2,3,20–23].

The information depth of the Si L_{2,3}VV Auger process is determined by the kinetic energy of the emitted Auger electrons (for the Si L_{2,3}VV Auger transition with a kinetic energy of about 92 eV) resulting in an inelastic mean free path length of a few atom layers. The termination of a silicon crystal along the (100) orientation usually results in a 2 × 1 reconstructed surface. In this paper we will show that the 2 × 1 reconstruction induces relatively large variations in the LDOS of the different types of surface atoms. Therefore, the kinetic energy distribution, $N(E)$, of the Si L_{2,3}VV Auger process will be sensitive to the geometrical structure of the silicon surface.

It has been shown that for covalent molecules, for example silicon, the interatomic Auger matrix elements can be neglected [10,21,24]. This extreme local behaviour of the Auger process enables us to model the half-infinite Si surface in terms of a finite cluster of silicon atoms. Quantum chemical cluster calculations performed in real space can be utilized to obtain the partial angular momentum dependent LDOS (pLDOS) of a surface silicon atom and calculate the pure, distortion free CVV Auger lineshape $A(E)$. One of the main advantages of this type of calculations is the possibility to evaluate the influence of the surface geometry on our lineshape analysis. We can construct the (100) surface by incorporating the 2 × 1 reconstruction related surface bonds, such as filled and empty dangling bond, dimer bond and backbond.

The aim of this paper is to present the calculated partial local density of states of the surface atoms of the clean 2 × 1 reconstructed Si(100) surface and the comparison of these calculations with the measured density of states obtained from the Si L_{2,3}VV Auger spectrum. A modification of the Mularie and Peria scheme for deconvolution of the broadening of the Si LVV Auger spectrum is presented.

This paper is organized as follows. In section 2 we will discuss the Auger measurements and the data processing required to obtain the density of states from the Si L_{2,3}VV Auger spectrum. The quantum chemical calculational aspects are explained in section 3. In section 4 we compare the calculated and measured density of states. Concluding remarks are given at the end of this paper.

2. Experimental

2.1. Equipment

The Si L_{2,3}VV Auger spectra were recorded under the following operational conditions: The primary electrons were accelerated to 2000 eV by a Wallis

PM4DCP (10-4000) high voltage unit; primary current density of 100 $\mu\text{A}/\text{cm}^2$; modulation of the RFA detector is 2 $V_{\text{p-p}}$; sweep rate between 0.05 and 0.5 eV/s. The Auger spectra were recorded between 15 and 115 eV in the more sensitive first derivative ($dN(E)/dE$) of the kinetic energy distribution of the Auger electrons by using a PAR lock-in amplifier with a lock-in time constant ≤ 1 s. The $dN(E)/dE$ Auger spectra were stored digitally.

The surface cleaning is performed by repeated argon sputtering (800 eV) and annealing at 600 °C during sputtering and annealing at 800 °C during 1 h after the sputter cycles [25]. The surface was considered to be clean when no elements other than Si could be detected in the Auger KLL spectrum. We estimate that the carbon surface concentration is about 0.001 monolayer or less [25].

2.2. Determination of the TDOS of clean Si(100)

The measured Auger lineshape appears as a convolution product of the local transition densities in the valence band for the two electrons involved, distorted by an escape function and all kinds of loss mechanisms, such as plasmon losses, secondary background, and instrumental broadening [13,14]. Assuming that an accurate correction for this distortion is feasible we can describe $A(E)$ as a summation over all Auger transitions with the same final state energy, each weighted with the Auger matrix element $|M(E_v, \Delta)|^2$ of the respective Auger process. Screening of the s-like valence band electrons of the core hole and final state shakeoff effects [3,10,20–23] are neglected:

$$A(E_v) = \int |M(E_v, \Delta)|^2 D(E_v - \Delta) D(E_v + \Delta) d\Delta. \quad (1)$$

Due to the localization of the core hole it is possible to write the Auger matrix element $M(E_v, \Delta)$ in terms of angular momentum dependent atomic Auger matrix elements localized at the same site as the core-hole.

The self-deconvolution of $A(E)$ with the assumption of constant atomic matrix elements across the valence band [6,7] can be interpreted as a transition density of states (TDOS). If the atomic matrix elements are known, then the TDOS can be interpreted as the LDOS, $D(E)$ [26–28].

Our (self-)deconvolution method [12,15,29] bypasses numerical problems such as the ambiguities of the square root of the complex phase in Fourier transforms [8,27,28] and the difficulties of the choice of the starting point of the sequential digital method developed by Hagstrum and Becker [6,7]. This method is based on global approximation using splines [30] and a modified non-linear least-squares fitting routine (Levenberg–Marquardt) [31]. In global approximation the line regions over the entire spectrum are correlated. This property is used to suppress uncorrelated frequencies, such as noise. This is achieved by constructing a trial function composed of spline and making an

approximation of the self-convolution of this spline function to $A(E)$. The sum of the squares of the difference between the spline function and the measured spectrum is minimized.

The self-deconvolution routine with splines [15,29] can guarantee that the obtained solution is continuous and real in contrast to Fourier transform based routines. The continuity of the solution is important for the physical interpretation of the result of the self-deconvolution [29].

2.3. Correction of the Auger lineshape

If one wants to perform an Auger lineshape analysis a careful correction of the distortions is necessary which requires a careful study of its nature (this is already discussed elsewhere [15]). We will give a brief review of the method used in this work.

The creation of the Auger CVV lineshape can be distinguished in three steps [1,10]:

- (i) A primary beam of electrons or photons (XPS) generates a corehole.
- (ii) A valence electron annihilates the core hole. The energy quantum gained by this relaxation process is used to eject another valence electron into vacuum. For core levels with binding energy higher than -5000 eV this radiationless relaxation is favoured over the creation of a Röntgen photon. The Auger decay leaves the atom in a doubly ionized final state.
- (iii) The Auger electron is scattered elastically and inelastically by the distorted surface charge distributions and the escaping Auger electron is distorted by the detection apparatus.

Neglecting the screening of the s-like valence band electrons of the core hole and final state shakeoff effects the Auger lineshape is mainly determined by step (ii) [2,10,12,22,23,26–28,32] and the distortions are due to the first and third step.

We use the following model, based on the concept of Mularie and Peria [14], with $*$ denoting the convolution operation, to describe the lineshape distortion:

$$N(E) = B(E) + I(E) * L(E) * P(E) * A(E) = B(E) + V(E) * A(E), \quad (2)$$

where $N(E)$ is the distorted measured spectrum and $A(E)$ the true distribution of the Auger electrons. $B(E)$ represents the secondaries from the incident primary beam. The correction for this background, $B(E)$, is easily made using the method of Seah [33] or Sickafus [34], based on the original calculations on metals by Wolf [35]. Mularie and Peria [14] introduced a method for simulating the total distortion, $I(E) * L(E) * P(E)$, ($I(E)$), extrinsic losses, $L(E)$, intrinsic losses and, $P(E)$, the broadening due to detection and signal processing by measuring the energy distribution, $V(E)$, of the reflection of a

primary electron beam. They assumed that the lineshape deformation is proportional to the energy distribution of a reflected beam of electrons with the same energy as the dominant Auger transition. This model is certainly not correct in the case of CVV Auger electron spectroscopy with C the lowest core level. Consider, for example, the Si L_{2,3}VV transition; the binding energy of the L_{2,3} level is about 104 eV and the main Auger transition occurs at 91.8 eV. A primary beam of 91.8 eV, which should model the loss-broadening function is however, not able to ionize the L shell. Moreover, it cannot induce a non-equilibrium distribution of the electrons which is inherent to the Auger process. In this case the reflected electron beam can only correct for the extrinsic losses $I(E)$ caused by the transport of the escaping Auger electrons through the condensed matter, and broadening of the detector $P(E)$. Due to the high surface sensitivity of the Si L_{2,3}VV Auger process the extrinsic loss features are very weak. This is supported by EELS measurements [36–38].

Electron beam reflection measurements at energies larger than $3E_c$, with E_c the energy of the lowest core level, show intrinsic inelastic scattering ($L(E)$) phenomena comparable to the loss phenomena observed in Auger electron spectroscopy (peaks at 74, 55 eV (fig. 1a)). The non-equilibrium distribution of electrons resulting from the excitation of a core hole, occurring at beam energies larger than $3E_c$, can give rise to additional collective oscillations which result in loss phenomena as described by Langreth [39].

The measurements of Gergely et al. [36,37] show a relation between the number of electrons in the n th plasmon loss feature N_{pl}^n and the number of electrons in the main peak N_{el} :

$$N_{pl}^n = \gamma^n N_{el}. \quad (3)$$

They found that the factor γ is constant over a large energy region of the incident electron beam (300–1800 eV). (For Si, $\gamma = 0.64$.) As the structure of inelastic scattering is only slightly dependent on the electron energy, $V(E)$ (fig. 1) can be measured as proposed by Mularie and Peria [14], but at energies at least $3E_c$, i.e. for Si > 300 eV. Therefore, a modification of the method as described by Mularie and Peria is made, by measuring the broadening function using a primary beam of 300 eV and thus ionizing the lowest core level of the silicon atom. Investigation of the distortion of the line profile as a function of the primary energy revealed that the difference in the absolute energy resolution of the RFA detector, with a modulation amplitude of $2 V_{p-p}$, is not significant for electrons with kinetic energies of 91.8 or 300 eV. This is in agreement with the results of Taylor [40].

However, using this method, there still exist uncertainties about the total removal of all intrinsic and extrinsic losses, and therefore care has to be taken in the analysis of the obtained spectrum.

The deconvolution of the kinetic energy distribution $dN(E)/dE$ and the energy loss function $dV(E)/dE$, obtaining the true kinetic energy distribu-

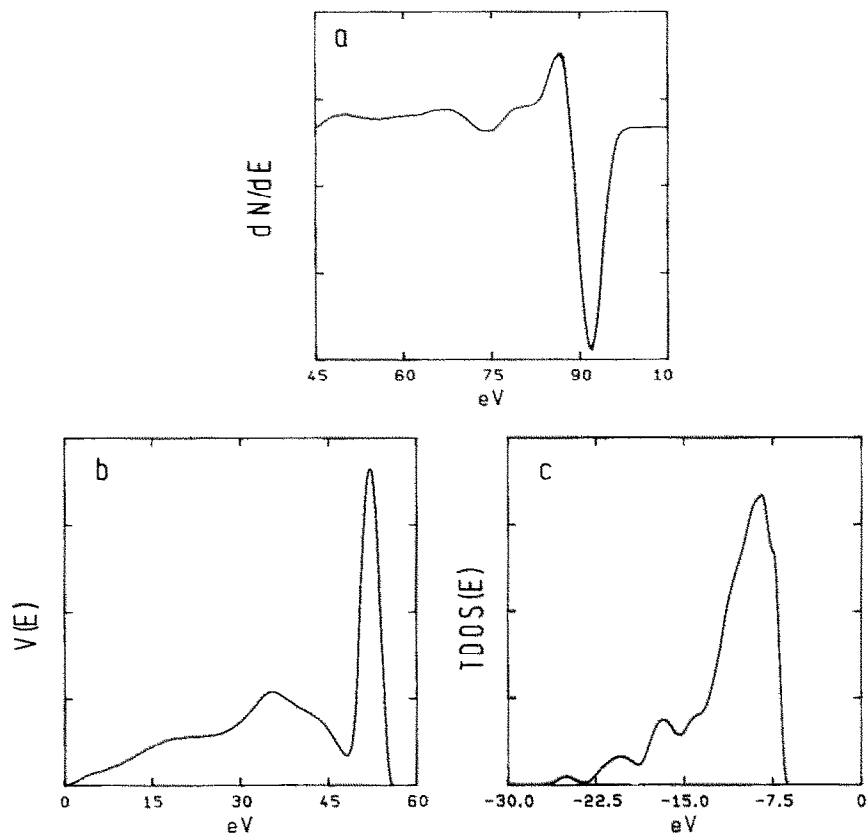


Fig. 1. (a) Si L_{2,3}VV Auger spectrum in the derivative mode of the clean Si(100)2 × 1 reconstructed surface. (b) The response function $V(E)$ (our deconvolution method operates on spectra in the derivative mode). (c) The TDOS (= the self-deconvolution of the loss corrected Auger lineshape $A(E)$). The zero level is the vacuum level.

tion, $A(E)$ is quite troublesome and far from trivial. The deconvolution method used is basically the same as the one applied to the self-deconvolution of $A(E)$ [12,15,29]. The TDOS curve obtained from the self-deconvolution of $A(E)$ and the measured spectra dN/dE and the integrated dV/dE , $V(E)$ are shown in fig. 1.

3. Method of calculation

Within the independent particle approximation and due to the core hole localization, Feibelman et al. [3], showed that the Auger lineshape can be expressed in terms of atomic Auger elements and of the angular momentum

components of the LDOS localized on the same site as the core hole. If the lineshape does not reflect the final state hole configuration, which is the case for s–p materials such as silicon [2,20–24], information of the local density of occupied states can be obtained. We can express the Auger lineshape in terms of convolution products of the pLDOS:

$$A(E) = C_{ss}D_s(E) * D_s(E) + C_{sp}D_s(E) * D_p(E) + C_{pp}D_p(E) * D_p(E), \quad (4)$$

C_{il} ($k, l = s, p$) are the atomic matrix elements and $D_k(E)$ are the k -like LDOS at the position of the atom in which the initial hole is produced.

We utilize a theoretical pLDOS, D_k , obtained from a semi-empirical quantum chemical cluster calculation. One of the main advantages using this kind of calculation is that we compute a real space pLDOS. This enables us to evaluate the influence of the Si surface related atoms, such as up and down atoms in the dimer (Si(100)2 × 1) or the second layer atoms connected to the up and down atom, on the Auger lineshape.

The LCAO-MO theory and its applications to molecules is well known [41,42]. For our calculations we have adapted the semi-empirical quantum chemical method MINDO/3 [43,44]. We briefly summarize some general formulations.

The molecular orbital ϕ_A is constructed by a linear combination of atomic orbitals χ_μ :

$$\phi_A = \sum c_{A\mu} \chi_\mu. \quad (5)$$

The coefficients are determined by the Roothaan–Hall equations [45], derived from the Hartree–Fock treatment:

$$FC = SCE, \quad (6)$$

where F is the Fock matrix, C the coefficients matrix, S the atomic orbital overlap matrix and E a diagonal matrix containing the atomic orbital energies ϵ_A . In the Fock matrix all three and four center integrals are neglected, and the two-electron two-center integrals depend only on the kind of atoms in question, and are independent of azimuthal quantum number of the atomic orbitals. The remaining two-center integrals will be set equal to parametric functions that can be adjusted to fit experimental data. The one-center integrals are estimated from spectroscopic values, according to Oleari's method [46].

In our calculation method the Si(100)2 × 1 reconstructed surface is represented by finite clusters. The MINDO/3 program is utilized to calculate the nature, i.e. the coefficients of the molecular orbitals and their orbital energy. It is stated that clusters containing 50 atoms or less, a number already beyond our possibilities, would be sorely inadequate for a discussion of a number of solid state aspects of the substrate [47]. However, the interest here is not in

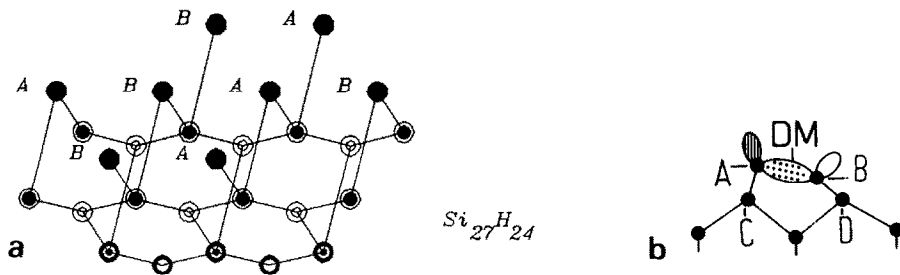


Fig. 2. (a) The Si₂₇H₂₄ cluster. The unsaturated Si bonds below the first layer are terminated with hydrogen atoms (for convenience not drawn here). The unsaturated surface Si bonds are subject to surface reconstruction and form dimer and dangling bonds. The reconstruction is denoted by A, B, with A the up atom and B the down atom of the dimer in the first layer. The values of refs. [49,50] have been used for the 2 × 1 reconstruction. (b) The reconstructed surface with a dimer bond (DM), with A the up atom, B the down atom, C the second layer atom bonded to the up atom and D the second layer atom bonded to the down atom.

reproducing bulk properties, but to understand local processes like the Auger process, which is localized mainly on one atom [2,10], situated in the first two atom layers. This is a very different task and is accessible through cluster studies [22,23].

The discrete local density of states at atom X is given by:

$$\rho_X^*(E) = \sum_A \left[\sum_{\mu}^X |c_{A\mu}|^2 \right] \delta(E - e_A), \quad (7)$$

where the summation μ runs over all atomic orbitals on atom X . The bulk influence is simulated by a broadening of the energy levels with gaussians, resulting in the LDOS:

$$\rho_X(E) = (\pi\sigma^2)^{-1/2} \sum_A \left(\sum_{\mu}^X |c_{A\mu}|^2 \right) \exp[-(E - e_A)/\sigma^2]. \quad (8)$$

The most commonly used value for σ is 1 eV [47,48], which in our case gives the most satisfying results. The LDOS can be split into its angular components (s, p), yielding the partial LDOS (pLDOS).

For our cluster modeling the Si(100)2 × 1 reconstructed surface we have used a Si₂₇H₂₄ cluster (see fig. 2a). For the subsurface atoms the ideal bulk geometry of silicon ($d_{\text{Si-Si}} = 2.35$ Å, and tetrahedral angles) has been used, whereas the surface atoms are subject to an asymmetric 2 × 1 reconstruction [49,50] as used by Kunjunny and Ferry [51]. In fig. 2b the reconstruction is depicted and the atoms for which the calculations are performed have been labeled.

It is important in the molecular environment to set appropriate boundary conditions in order to avoid generating fictitious surface states which could

interact with the real surface states, thus severely affecting the final results [52]. We used hydrogen atoms to terminate the silicon substrate to obtain boundary conditions of sufficient quality. The value attributed to the Si–H bond length has been subject of debate [52,53]. We have adapted the most recent value $d_{\text{Si-H}} = 1.41$ Å found by Estreicher [53].

Kunjunny and Ferry, using a tight-binding method, showed that the nearest and second nearest neighbour interactions are adequate to describe the local electronic properties. This condition can be easily fulfilled in our cluster approach. The atomic positions and bond lengths were taken to agree with the known average values [49–51]. The exact atomic positions of the silicon atoms could be obtained from energy minimizing calculations or diffraction experiments. Small changes in atomic positions and bond lengths were found to produce negligible changes in the results.

4. Results and discussion

The results of the calculations and measurements are depicted in figs. 3 and 4 and table 1. In fig. 3 we plotted, respectively, the LDOS and the pLDOS of the up (a) and down atom (b) of the dimer in the first layer and the second layer atoms bonded to the up (c) and down (d) atom. In the measured TDOS, fig. 4, we resolve the transitions labeled A to E at -8.4 (a), -13.4 (b), -16.2 (C), -19.9 (D), -24.2 eV (E) and shoulders at -7.1 (A₁) and -13.6 eV (A₂) with respect to vacuum. Peaks D and E are resolved for the first time with AES. Both peaks are also resolved in our calculations (-20.4 and -24.2 eV) and support their significance (table 1). The work function for Si(100) surface is 4.9 ± 0.1 eV [54]. This value is used for the shift of the energy scales from valence band maximum (VBM) to vacuum level. We have used the vacuum level as zero point in the representation of our results because this is an absolute zero point in contrast to the quite arbitrary valence band maximum. The results from literature as shown in table 1 are therefore shifted to our zero point.

Our calculated results show good agreement with calculated results published in earlier work [3,51,55]. However, we calculate with our cluster approach high binding energy levels in the LDOS (-24.2 (E), -27.7 eV (F)). These very localized Si 3s levels are not reported in *k*-space orientated solid state density calculations [51,55–58], since this type of calculation has difficulties in describing very localized levels. These levels could be interpreted as more atom-like energy levels due to the symmetry breakdown of the crystalline electronic bulk structure at the surface. It is difficult to resolve these peaks experimentally, therefore their existence is a matter of debate although we did resolve a peak (E) in our measured TDOS.

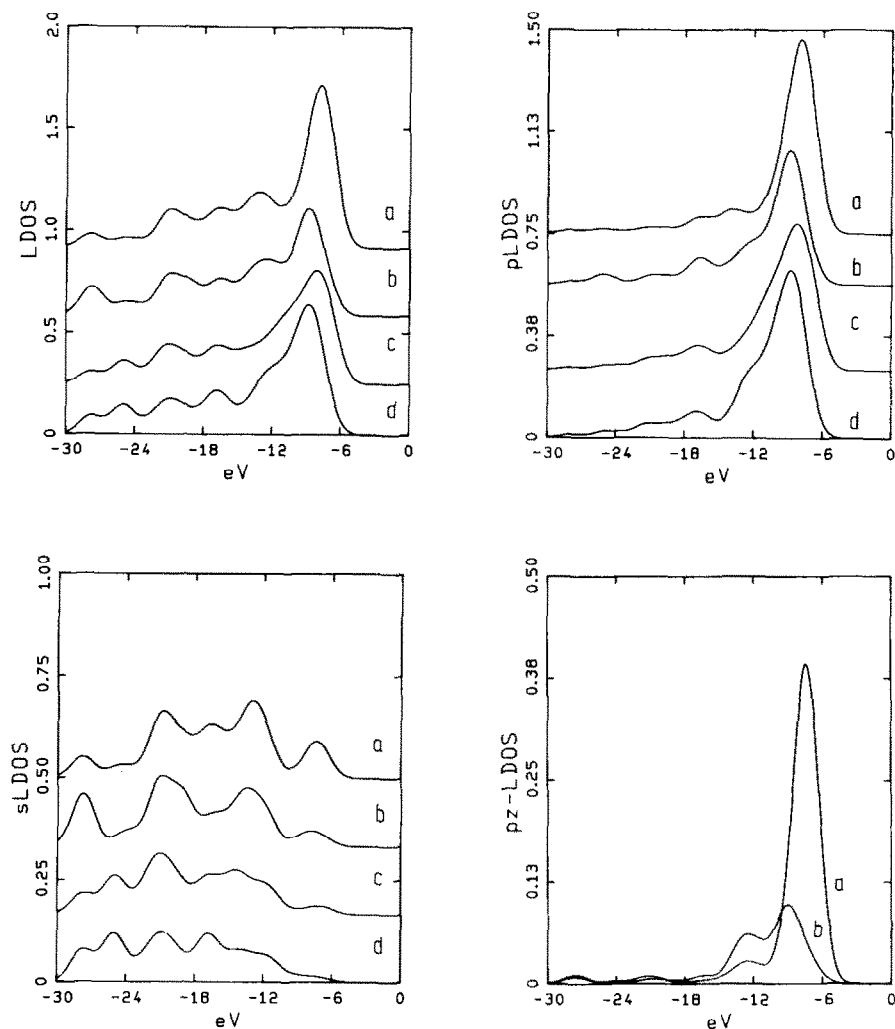


Fig. 3. The calculated LDOS and the s, pLDOS of the Si₂₇H₂₄ cluster. The densities are calculated from the Si atoms at the top. In all figures we denote: (a) up atom; (b) down atom; (c) second layer atom bonded to the up atom; (d) second layer atom bonded to the down atom. LDOS (left top); p-type LDOS (right top); s-type LDOS (left bottom); p_z-type LDOS (right bottom). The vacuum level is the zero of the energy scale.

Another significant difference between our calculations and *k*-space calculations can be seen at about -13 eV. This feature can be attributed to σ -bonding of the dimer resulting in a 2 × 1 reconstruction of the surface silicon atoms. This is in agreement with the calculations of Ciraci et al. [59]. Furthermore, our calculations show a more s-type surface with respect to the

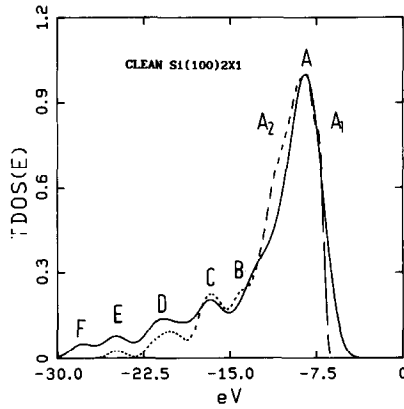


Fig. 4. Solid line: the calculated LDOS. This LDOS is the summation of the LDOS of the surface atoms in the first two atom layers (fig. 3), which is consistent with the probing depth of the Auger process. Dashed line: the experimentally derived TDOS of the clean Si(100)2 × 1 reconstructed surface (fig. 1c). The vacuum level is the zero of the energy scale.

bulk. This is also reported by others [50]. We also see that the influence of the LDOS of the silicon atoms in the second layer due to bonding to the up or down atom of the dimer is almost negligible (figs. 3c and 3d), suggesting a rapid convergence to the bulk LDOS.

Upon comparing the peak positions of the TDOS spectrum, obtained with the assumption that the Auger matrix elements do not vary with energy across the valence band, with the calculated weighted LDOS, the validity of the approximation is supported that the Auger matrix elements do not shift peaks significantly and modulate only the intensity of the LDOS. The modulation of the intensity of the LDOS will be, predominantly, a function of the angular momenta of the electrons involved in the Auger process. Using the same procedure as Zajac and Bader [60] we introduce a parameter α , which takes into account the angular momentum weighting of the Si 3s band with respect to the Si 3p band.

$$D_{\text{Si}}(E) = \alpha D_{3s}(E) + D_{3p}(E). \quad (9)$$

More rigorously, two parameters should be used, one for the ss and one for the sp terms, but the above parameterization has proven to be adequate [3,20,21]. We improve the fit between experiment and calculation by an appropriate choice of α ($= 0.255$). This value is derived from the C_{ss} Auger matrix element obtained by Jennison [20,21].

Comparing the measured (fig. 4) with the calculated results (fig. 3), using eq. (9), peak A can be attributed to p-type valence electrons of the up, down and second-layer atoms. We see also a significant contribution of the s-type

Table 1
Peak positions of the valence band of Si(100)2 × 1 (the vacuum level has been taken as zero point)

Authors	Method	Peaks (eV)								
		A ₁	A	A ₂	B	C	D	E	F	
Feibelman and McGuire [3]	Calc.		-8.8		-13.3	-16.4				
Pandey and Philips [55]	Calc. ^{a)}		-8.8		-13.3	-15.5				
Kunjunny and Ferry [51]	Calc. ^{a)}		-8.4		-12.9	-15.4				
This work	Calc.	-7.5	-8.4	-11	-12.9	-16.2	-20.4	-24.4	-27.7	
This work	LVV	-7.1	-8.4	-11.6	-13.4	-16.2	-19.9	-24.2		
Houston et al. [19]	LVV		-9.0							
Rowe and Ibach [38]	EELS	-7			-13		-20			
Hollinger and Himpfel [61]	UPS		-8.7		-12.9	-14.9				
Yin and Cohen [56]	Calc. bulk		-7.8		-11.9	-14.4				

^{a)} Only the main features are tabulated.

electrons from the filled dangling bond which agrees with ref. [59], where it is argued that the up-dangling bond is composed primarily of $s + p_z$ orbitals.

Calculations predicted features at -13.0 eV, which can be interpreted as an s -type valence electron forming a dimer bond. This peak, labeled B, is in our calculations very sensitive to positions of the reconstructed first layer atoms and thus for the cluster geometry. We resolve experimentally a peak at about -13.4 eV which may be attributed to this transition. The small difference in the peak position between the experimental and calculated results can be explained by the overlap of this peak with the not fully corrected bulk plasmon loss peak in the Auger spectrum ($dN(E)/dE$) at 74 eV.

Peak C is composed of contributions of s and p -type orbitals of the up, down and second layer atoms. We see that the second layer atom and the up atom have a more s -type contribution to this energy level than the down atom. Also can be recognized the $p_{x,y}$ contribution of the second layer atoms and the down atom are more dominant than the $p_{x,y}$ contribution of the up-dimer atom.

Peak D is only reported in EELS spectra of Rowe and Ibach [38], since in UPS measurements using HeI or HeII sources, high binding energy levels below -20 eV are not well resolved due to the large secondary background and lack of surface sensitiveness [54]. Ciraci et al. [59] stated that “neither of the UPS spectra gives any indication about the strong dimer peak at -13 eV, which was produced in several calculations [49,57], thus raising the question of the appropriateness of this technique for high binding energy levels situated at the first two atom layers”. They observed this -20 eV transition for both crystalline and sputtered surfaces (100, 111, 110) [38], an observation which gives rise to speculation that second layer atoms are related to this peak. This suggestion is supported by our calculations. Identifying the peak at -20.4 eV in our calculations with the peak of -19.9 eV in the TDOS we see that the contribution of the four types of surface atoms is almost equal and is completely composed of s -type orbitals. Furthermore, testing the convergence of the LDOS as a function of the cluster size we noticed that this peak is insensitive upon changes in the cluster geometry. Based on these facts we interpret peak D as a Si–Si bond between first and second layer atoms of s -type valence electrons.

The transition E is predominantly composed of contributions of s -type electrons localized at the second layer atoms. This peak has not been reported in earlier investigations and supports the suggestion of high binding energy levels of valence electrons at surface atoms.

We can also resolve two shoulders in the measured TDOS (A_1 and A_2). Care need to be taken to ascribe these structures to physically significant features, because of the extensive data processing involved in obtaining the TDOS. Nevertheless, we will try to explain these features. Firstly, we could ascribe the shoulder A_1 to the p_z -LDOS of the up atom in the dimer (bottom

right fig. 3). We see that this dominant peak in the LDOS is shifted with about 1 eV to the vacuum level. This shift is also present at the p_z-LDOS of the second layer atom connected to the up atom in the dimer. The broadening of the discrete energy levels by gaussians ($\sigma = 1$ eV) obscures this feature in the LDOS. Secondly, the shoulder A₂ could possibly be identified with the shoulders in the pLDOS of the second layer atoms and the down atom of the dimer at about -13 eV or to a not fully corrected lineshape.

High binding energy levels below -20 eV (relative to VBM), as revealed by our calculations, could not be resolved in the Si L_{2,3}VV spectra, since this part of the spectrum overlaps with the Coster-Kronig Auger transition (L₁L_{2,3}V) [62]. This could be a reason why the calculation of the Auger matrix elements for L₁L_{2,3}V Auger transitions does not fit well with experimental results [3] and may explain why the lineshape of L₁L_{2,3}V spectra are broader than one would expect on the basis of X-ray photoelectron spectroscopy measurements of 2s hole widths [3]. Stankiewicz reported also deep lying valence levels in her calculation of surface states using a LCAO method [63].

5. Concluding remarks

We have shown that care need to be taken in the choice of the response function, $V(E)$, when the kinetic energy of the primary excitation is comparable to the lowest lying core level. Utilizing this improved response function we modified the scheme of Mularie and Peria for the correction of the measured Auger lineshape for elastic and inelastic scattering. The TDOS resolved a fine structure with several new peaks compared to previous AES measurements as well as to UPS and EELS measurements.

Quantum chemical cluster calculations were able to produce partial LDOS localized at atoms of the Si(100) surface, which was subject to a 2 × 1 reconstruction. The results of the calculation were in agreement with those of other investigators. The agreement of the peak positions of the calculated LDOS with experimental results shows the potential power of this type of cluster calculations to obtain information of valence electron energy levels of surface atoms, and a more unambiguous characterization of peaks in the AES spectrum has been achieved.

It is shown that surface geometry varies the partial LDOS significantly and therefore influences the Si L_{2,3}VV Auger spectrum. Moreover, features in the measured TDOS spectrum could be localized at different surface atoms.

Quantum chemical calculations used routinely in chemical physics can be adapted for modeling local phenomena in half-infinite materials, e.g. semiconductors such as silicon. Moreover, the overall agreement with results reported in literature legitimizes its use for further analysis of Auger measure-

ments and makes a new step in the application of AES in the study of the surface chemical bond.

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